

## Master equation approach to viscous liquids and the glass transition

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*Publication date:*  
1988

*Document Version*  
Publisher's PDF, also known as Version of record

*Citation for published version (APA):*  
Dyre, J. C. (1988). *Master equation approach to viscous liquids and the glass transition*. Roskilde Universitet.

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# TEKST NR 154

# 1988

MASTER EQUATION APPROACH TO VISCOUS LIQUIDS AND THE  
GLASS TRANSITION

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INSTITUT FOR STUDIET AF MATEMATIK OG FYSIK SAMT DERES  
FUNKTIONER I UNDERVISNING, FORSKNING OG ANVENDELSER

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IMFUFA tekst nr. 154/88

55 pages

ISSN 0106-6242

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Abstract:

Denne artikel handler om en fænomenologisk model for tyktflydende væsker og glasovergangen. Et mere udførligt abstract finder man på side 1.

# 1

## ABSTRACT

By arguing inductively from experiment a simple picture of atomic motion in viscous liquids is arrived at, according to which the liquid flows by sudden cooperative rearrangements of atoms in a "region" of the liquid. A region is a thermodynamic system, i. e. has a density of states  $n(E)=\exp(S(E))$  with  $\frac{\partial S}{\partial E} > 0$  and  $\frac{\partial^2 S}{\partial E^2} < 0$ , where by a state is meant a potential energy minimum. A master equation describing the region energy fluctuations is derived by assuming a region forgets which state it came from, once it is excited into the transition state. The master equation allows a detailed discussion of linear and non-linear relaxation phenomena and of the glass transition. For linear relaxation in the equilibrium liquid, it is shown that the loss peak is simply related to the entropy function  $S(E)$ . Non-linear relaxation is studied by solving the master equation for a sudden change of temperature from thermal equilibrium to a lower temperature, and also to a higher temperature. In the first case, the energy probability distribution adjusts continuously towards equilibrium, whereas in the second case the states "evaporate" in the course of the relaxation and thermalise immediately thereafter. There are two different kinds of glass transition according to the model, depending on the cooling rate and on the region specific heat at  $T_g$ . A slow glass transition freezes-in the equilibrium gaussian energy distribution. In the case of a fast glass transition, relaxation phenomena at  $T_g$  are important and the resulting frozen-in energy distribution is an exponential. Finally, it is pointed out that a glass may also be prepared by a quench, an "infinitely" fast cooling, which should be distinguished from a glass transition where there is a gradual

falling out of equilibrium during the cooling.

## 1. INTRODUCTION

The glass transition takes place when a liquid upon cooling becomes more and more viscous and finally solidifies to a glassy solid [1-17]. Most, or perhaps all, liquids are able to form glasses when cooled sufficiently fast to avoid crystallisation. Examples of glasses include the classical oxide glasses, metallic glasses, ionic glasses, polymers, and glasses made by cooling organic liquids to low temperatures. Even simple liquids such as argon have been found able of glass formation in computer experiments, so the glass transition seems to be a universal phenomenon. It has been studied for many years but is still not well-understood. The only thing universally agreed upon is the kinetic nature of the glass transition. Though thermodynamically similar to a second order phase transition, the glass transition is not a phase transition in the ordinary sense. This is evidenced by several facts: The transition is not sharp, the transition temperature  $T_g$  depends on the cooling rate, and the transition is irreversible and has various hysteresis phenomena associated with it. The kinetic nature of the glass transition complicates the problem since a proper model must be based on a detailed picture of the dynamics involved. To make things even worse, the viscous liquid itself is usually not in true thermodynamic equilibrium, because, below the melting temperature, the crystal phase has lower free energy. A first principles statistical mechanical calculation thus inevitably brings one to the crystalline phase without any sign of glass formation, a fact which seems to favour a more phenomenological approach. It is the purpose of this paper to present a simple

phenomenological picture of viscous liquids and the glass transition, based mainly on plausibility arguments.

In many discussions of the glass transition prominent roles are played by the Kauzmann paradox [2] and the Vogel-Fulcher law [18]. The Kauzmann paradox, which was actually first discussed by Simon [1], is the fact that the super-cooled liquid entropy, when extrapolated beyond  $T_g$ , falls below the crystal entropy at a temperature  $T_K > 0$ . Usually,  $T_K$  lies only about 50 K below  $T_g$  [12,19]. The purely vibrational entropy of the liquid is close to the crystal entropy as evidenced by similar sound velocities in the glassy and crystalline phases. Therefore, either the equilibrium liquid cannot exist below  $T_K$  or the extrapolation is incorrect; this is the paradox. The Vogel-Fulcher law is the following expression for the average relaxation time of a viscous liquid

$$\tau = \tau_0 e^{\frac{A}{T-T_0}} \quad (1)$$

The average relaxation time can be determined e. g. as the inverse dielectric or mechanical loss peak frequency, or it may be calculated from the viscosity  $\eta$  by means of

$$\tau = \frac{\eta}{G_\infty} \quad (2)$$

where  $G_\infty$  is the infinite frequency shear modulus. These definitions do not give exactly identical  $\tau$ 's but the difference is insignificant for the present discussion. The Vogel-Fulcher law gives a good fit to many experiments with the characteristic temperature  $T_0$  often quite close to the Kauzmann temperature [20,21]. From this one may argue that there is a

genuine phase transition of the equilibrium viscous liquid at  $T=T_0$  to an "ideal" glassy solid with zero configurational entropy, a state of matter which can however only be reached by infinitely slow cooling. This is the basic idea of the entropy theory of Gibbs and co-workers [19,22]. Another phase transition theory is the free volume model [23]. Ideas of a phase transition underlying the glass transition have also gained support from calculations applying the sophisticated techniques of modern liquid theory [24,25,26], and from the theory of spin glasses [27].

Though attractive, we feel there is no compelling evidence for the idea of an underlying phase transition. The original theoretical arguments for it has more recently been shown to be incorrect [28], and as regards experimental evidence the Kauzmann paradox does not have to be a paradox. It is possible that the extrapolation of the liquid entropy beyond  $T_g$  simply is incorrect. As pointed out by Angell and Rao, even the simplest conceivable statistical mechanical system, that with only two energy levels, has an entropy which, if only known at high temperatures, extrapolates to zero at a positive temperature [20]. Their model does not fit all experiments, but the excess entropy data may be reproduced in models with a finite number of energy levels and thus without any phase transition [29]. -- While the Kauzmann paradox remains intriguing, the Vogel-Fulcher law simply does not apply in the whole temperature range of interest. This has been known for many years [30-33] but is still not generally appreciated. Deviations from eq. (1) occur for large viscosities where the data are always less temperature dependent than predicted. This is exactly where eq. (1) becomes most interesting, thus questioning an important argument for



phase transition theories. Instead of eq. (1), the data may be fitted by letting  $T_0$  vary with temperature [30], or by an expression of the form  $\tau \propto \exp(A/T^n)$  where  $n > 1$  [34]. The case  $n=2$  is particularly interesting; it fits many data and has some theoretical justification being derivable from the assumption of a gaussian distribution of activation energies [35].

Glasses are formed from viscous liquids so a better understanding of glasses and the glass transition must derive from a better understanding of viscous liquids [36,37]. The necessity of focusing on viscous liquids has been emphasised in particular by Goldstein. In his view, the problem of the glass transition is just an aspect of the problem of the liquid state and a theory of the glass transition and the glassy state will be a by-product of a theory of liquid viscosity [29,36]. Thus, initially one should focus on understanding viscous liquids in thermal equilibrium and forget about the glass transition, although this is the subject of real interest. The problem of describing equilibrium viscous liquids also must be much easier than to describe glasses, since a full knowledge of the state of a glass requires a specification of its entire thermal history after reaching  $T_g$  while a liquid is characterised by just temperature and pressure.

The simplest approach to the viscous liquid problem is to extrapolate the theory of simple liquids to low temperatures. This was done in 1984 by Leutheusser [24] and by Bengtzelius, Götze and Sjölander [25]. They showed from mode-coupling theory that the viscosity diverges at a finite temperature thus implying higher and higher viscosities upon cooling which eventually leads to glass formation. However, the theory predicts a power-

law divergence of the viscosity which does not fit experiment [38], and it has now been shown that the approximation scheme used in refs. [24,25] breaks down in the region of high viscosity [39,40].

Since the viscosity of glass forming liquids is  $10^{10}$  or more times larger than that of simple liquids, it is likely that the approximations needed to calculate the viscosity from the Hamiltonian are completely different from those appropriate for simple liquids [36]. According to this point of view, viscous liquids are qualitatively different from simple liquids [36,41,42]. There is actually experimental evidence for this. For instance, Brillouin linewidths, ultrasound absorption, and magnetic resonance in highly viscous liquids behave in a way which cannot be adequately explained by hydrodynamics [43]. Another indication of a qualitative shift going from the less viscous to the highly viscous regime has been investigated by Torell. For measurements on ionic liquids, she found at high temperatures and corresponding low viscosity an Arrhenius temperature dependent viscosity and simple exponential relaxation, which is lost in the same temperature range where the viscosity becomes non-Arrhenius [44]. Similar results have been reported for  $B_2O_3$  [45].

The present paper starts with a discussion of the nature of viscous flow in highly viscous (henceforth just: viscous) liquids. A picture is advanced where flow takes place via sudden cooperative rearrangements of the liquid atoms (the basic constituents of liquids will be referred to as atoms though they may be as well ions or molecules). Next follows a discussion of the temperature dependence of the activation energy  $\Delta E$  for the "flow events". It is shown that the naive way of evaluating

AE from experimental data most likely is wrong. By assuming the simplest possible collective dynamics, a master equation for the energy fluctuations is arrived at. This equation forms the basis for discussing linear and non-linear relaxation phenomena. It also allows a detailed discussion of the glass transition, a short report of which has been published elsewhere [46]. It turns out that there are two different kinds of glass transition, depending on the cooling rate. As a consequence, in general it is not correct to regard a glass just as a frozen liquid with the structure of the equilibrium liquid at  $T=T_g$ . The final section summarises and discusses the model. It is shown that there are serious discrepancies between theory and experiment; at present the theory is incomplete and further work is needed to make it realistic. However, the model does reproduce a number of characteristic features of viscous liquids and the glass transition, including the correlation between the width of the relaxation time distribution, the non-Arrhenius temperature dependence of the average relaxation time, and the excess specific heat of the supercooled liquid relative to the crystal [12]. Also, the model gives a simple picture of glassy relaxation.

The model of viscous liquids proposed here is inspired by Brawer's work [13,47]. He discussed neither linear relaxation nor the glass transition, however, and there are important differences in the roles played by activation energy and by activation entropy in the two models. In these respects the present work is closer to ideas put forward by Goldstein in 1972 [29] which were never developed further.

## 2. VISCOUS LIQUIDS IN THERMAL EQUILIBRIUM

The basic problem in viscous liquid theory is to identify the mechanism of viscous flow. Below, a phenomenological approach is adopted by limiting the discussion to the much simpler question: How do atoms in viscous liquids move at all? A simple picture of atomic motion is arrived at by arguing inductively from experiment, which is done to ensure only the minimum of assumptions are made.

As evidenced e. g. by dielectric relaxation experiments, the average relaxation time  $\tau$  is a direct measure of the time needed for atomic rearrangements. Typical values of  $\tau$  for glass forming liquids lie in the millisecond, second or even hour range, which is to be compared with the average vibration time of order one picosecond. It is hard to model this without assuming the atoms are caught in deep potential energy minima where they vibrate millions and millions times before, by thermal activation, suddenly rearranging into another potential energy minimum. Such a "flow event" does not involve the entire liquid, of course, but is highly localised. The idea of viscous flow occurring via flow events is old [8,13,19,36,41,48, 49]. Describing the dynamics by transition state theory [41,50], the heat bath is provided by the fast degrees of freedom. These are the momentum coordinates and also the vibrational contribution to the potential energy, where the potential energy is imagined to be separated into vibrational and configurational contributions. Note that this is a phenomenological distinction which does not correspond to a separation of the Hamiltonian into two terms. A potential energy minimum is henceforth referred to as a state, and by the energy of a state is meant the configurational part of

the potential energy, i. e. the value at the minimum.

As mentioned in the introduction, the average relaxation time usually has a non-Arrhenius temperature dependence. To look closer into this one plots  $\ln(\tau)$  as function of the inverse temperature, as shown in fig. 1. This plot is useful because it yields a straight line if  $\tau$  is simply activated. Typical data above and below  $T_g$  are shown, the latter derived from long time studies of glassy relaxation. The naive interpretation of the observations is the following (fig. 1a). It is assumed that  $\tau$  has a temperature dependent activation energy  $\Delta E(T)$  which is given by the slope of the tangent at  $T^{-1}$  (Boltzmann's constant is put equal to unity). The intercept of the tangent with the y-axis is also temperature dependent. This must be due to a temperature dependent activation entropy if the usual expression,

$$\tau = \tau_0 e^{-\Delta S} e^{\Delta E/T} \quad (3)$$

where  $\tau_0$  is of order 1 picosecond, is assumed to apply. The activation energy increases as  $T$  approaches  $T_g$  from above, while right at  $T_g$  there is a discontinuous change in activation energy to a lower, constant value. This is interpreted as being due to the fact that below  $T_g$  relaxation takes place in an essentially fixed structure, while above  $T_g$  the activation energy has an additional contribution from structural changes. The fact that  $\Delta S$  is large for the liquid close to  $T_g$  is taken as evidence of a cooperative nature of atomic motion in viscous liquids, while glassy relaxation must be less cooperative.

There are serious problems, however, with this picture. Given eq. (3), there is no reason  $\Delta E(T)$  should equal the slope

of the tangent which is given by

$$\frac{d \ln \tau}{dT^{-1}} = \Delta E(T) + T^{-1} \frac{d \Delta E}{dT^{-1}} - \frac{d \Delta S}{dT^{-1}} \quad (4)$$

For the last two terms to cancel  $\Delta S$  must be a function of  $\Delta E$  while in general  $\Delta S$  may vary independently of  $\Delta E$ . Thus  $\Delta E$  is generally different from the slope which should rather be referred to as the "apparent activation energy" [13,50].

Basically, the problem is that it is not possible to determine the two functions  $\Delta E(T)$  and  $\Delta S(T)$  just from  $\tau(T)$ . Some assumption must be made before useful information may be extracted from  $\tau(T)$ . We here assume that

$$\Delta S = 0. \quad (5)$$

The activation energy is then the slope of the secant drawn between  $(0, \ln(\tau_0))$  and  $(T^{-1}, \ln(\tau))$ , as illustrated in fig. 1b. Just as in the naive picture,  $\Delta E$  increases as  $T$  approaches  $T_g$  from the liquid side. But glassy relaxation is now interpreted differently. What happens at  $T_g$  is not a discontinuous change in activation energy, but that the activation energy stops changing with temperature. In support of this picture based on eq. (5), we note that glassy relaxation indeed has often a preexponential of order 1 picosecond [51,52,53].

Referring to the part of the liquid where a flow event takes place as a region, we now argue that a region must contain many atoms, implying a flow event is a cooperative process. If the energy maximum to be overcome is assumed to be temperature independent and equal to  $E_0$ , one has  $\Delta E(T) = E_0 - E_{min}(T)$  where

$E_{min}(T)$  is the energy at the minimum. As  $T$  approaches  $T_g$  from above,  $\Delta E$  increases so  $E_{min}(T)$  decreases. From the definition of  $T$  in terms of the dielectric loss peak maximum, it is clear that  $E_{min}(T)$  is the most likely region energy. For it to be an increasing function of temperature, the region must be a thermodynamic system, i. e. have a density of states,  $n(E)$ , obeying

$$n(E) = e^{S(E)}, \quad \frac{\partial S}{\partial E} > 0, \quad \frac{\partial^2 S}{\partial E^2} < 0. \quad (6)$$

The most probable energy in a thermodynamic system is close to the average energy,  $\bar{E}$ . Thus, the average relaxation time activation energy is given by

$$\Delta E(T) = E_0 - \bar{E}(T), \quad (7)$$

i. e. it is just the average activation energy as one might naively have guessed. But the requirement of eq. (6) is highly non-trivial. For instance, a two-level system or any system with equally spaced energy levels is not thermodynamic. The prototype of a thermodynamic system is one where the energy is a sum of several independent terms. Thus, for a region to be thermodynamic it must be larger than the "correlation length" for potential energy. This implies the dynamics of viscous liquids is cooperative. Many workers in the field have assumed cooperativeness of flow events, but based on different arguments [8,13,19,29,36,47,49,54,55]. As a simple example of a cooperative model, suppose a region consists of several subsystems with each only two energy levels, where, however, the dynamics involves exciting all subsystems simultaneously

[47,56]. This may be termed the gaussian model since the density of states for a region is a gaussian. If  $E_0$  lies in the middle of the gaussian, it is easy to show that  $\tau \propto \exp(A/T^2)$ . The gaussian model extends the simple thermodynamic model of Angell and Rao [20] to include dynamics in a way that fits many experiments [35].

In the naive picture of fig. 1a, the so-called preexponential of  $\tau$  is  $\exp(-\Delta S)$  where  $\Delta S$  is the activation entropy. In the approach advanced here  $\Delta S=0$  and the preexponential is instead  $\exp(-c)$  where  $c$  is the region specific heat. This follows from eq. (7) which implies the slope of the tangent is given by

$$\frac{d \ln \tau}{d T^{-1}} = \frac{d}{d T^{-1}} \left( T^{-1} \Delta E(T) \right) = \Delta E(T) + T c(T). \quad (8)$$

Note that only when  $c=0$  does a straight line in the Arrhenius plot correspond to a simply activated process. In general, a straight line signals a constant specific heat and the slope of the line is not the activation energy but  $E_0$ , the zero temperature activation energy (assuming  $\bar{E}(T=0)=0$ ).

Goldstein has suggested the transition state is the high-temperature, more-fluid liquid where the atoms are no longer trapped in a potential energy minimum [29]. Excitations to this state may be thought of as a local melting process, although this is not consistent with eq. (5). Brawer imagines the flow event to take place when a density fluctuation transforms a region to a state of small density where the atoms shuffle about for a short time before settling in a new potential energy minimum [47]. No matter what is the exact nature of the transition state, however, given the cooperative nature of flow events it seems reasonable



to assume that, once excited into the transition state, a region has forgotten where it came from and may end up in any other state. There is actually direct experimental evidence for this, coming from a comparison of dielectric and Kerr-effect measurements on a number of viscous liquids [49,57]. These experiments show that dipole reorientation occurs by sudden jumps to random new orientations and does not take place by rotational diffusion.

From the assumption that that an excited region jumps into a randomly chosen state, it is straightforward to derive the equation governing the dynamics. The only relevant degree of freedom is the region energy  $E$ . If the region energy is assumed to vary between zero and  $E_0$ , the equation for the time evolution of the energy probability density,  $P(E,t)$ , is

$$\frac{\partial P(E,t)}{\partial t} = -\frac{P(E,t)}{\tau(E)} + n(E) \int_0^{E_0} \frac{P(E',t)}{\tau(E')} dE' \quad (9)$$

where  $\tau(E)$  is given by

$$\tau(E) = \tau_0 e^{\frac{E_0 - E}{T}} \quad (10)$$

and  $n(E)$  is the normalised density of states. The first term on the right hand side of eq. (9) is the exponential decay of the probability due to jumps away from energy  $E$ . The second term reflects the fact that the probability of an excited region jumping into a state of energy  $E$  is proportional to the number of such states. The constant of proportionality is determined by requiring conservation of probability. An equation similar to eq. (9) has been used for describing the thermalisation of photo-excited charge carriers in amorphous semiconductors [58,59]. In

this case,  $n(E)$  is the density of trapping levels in the band gap and  $E_0$  is the mobility edge of the conduction band.

Equation (9) is almost the simplest conceivable for describing cooperative dynamics. Still, the physics contained in it is far from trivial. The equilibrium solution of eq. (9) is  $P_{eq}(E) \propto n(E) T(E)$  which is the canonical ensemble solution required by statistical mechanics. It comes about in the following way. From the assumption of jumping into random states, it is clear that on the average all states are visited equally often. The time spent in each state is proportional to the Boltzmann factor (eq.(10)), thus giving the correct weighting. Consider now the actual fluctuation in time of the region energy. Since  $n(E)$  is exponentially increasing, it is almost certain that, once a region has jumped, it ends up in a state with energy close to  $E_0$ . But if close to  $E_0$  it will spend only very little time in that state before jumping again. After a lot of similar "noisy" jumps close to  $E_0$ , the region eventually jumps to a low energy state where much longer time is spent. In this way the canonical ensemble is realised in time, determining at each temperature the most probable energy which is almost the same as the average energy  $\bar{E}(T)$ .

## 3. LINEAR RELAXATION PHENOMENA

In this section linear relaxation is discussed based on eq. (9). The example considered is dielectric relaxation but a similar treatment applies for e. g. mechanical relaxation. Indeed the present model implies all linear relaxation phenomena have identical response functions. This is not true in reality but is a consequence of the simplicity of the model.

According to the fluctuation-dissipation theorem, the linear response to an external field is determined by fluctuations in thermal equilibrium. The frequency-dependent dielectric constant,  $\chi(\omega)$ , is the Laplace transform of  $\frac{d}{dt} \langle P(0)P(t) \rangle$  evaluated in  $s = -i\omega$ , where  $\langle P(0)P(t) \rangle$  is the thermal equilibrium dipole moment autocorrelation function [60]. Since a region forgets where it came from once it jumps,  $\langle P(0)P(t) \rangle$  is proportional to  $\langle \exp(-t/\tau') \rangle$  where the average is over the distribution of relaxation times  $p(\tau')$ . When substituted into the Kubo formula for  $\chi(\omega)$ , this yields the well-known expression

$$\chi(\omega) = \chi(0) \left\langle \frac{1}{1 + i\omega\tau'} \right\rangle \quad (11)$$

where, however, the relaxation time has here a definite physical interpretation as the lifetime of a region in a state. The average in eq. (11) is dominated by contributions from  $\tau' = \omega^{-1}$ . Being mainly interested in the dielectric loss,  $\chi''(\omega)$ , this may be rationalised by replacing  $\omega\tau' / [1 + (\omega\tau')^2]$  by  $\frac{1}{2} \delta(\omega\tau' - 1)$  when the distribution of relaxation times is broad. Thus

$$\chi''(\omega) = \frac{1}{2} \chi(0) \omega^{-1} p(\tau'), \quad \tau' = \omega^{-1}. \quad (12)$$

The dielectric loss may be related to thermodynamics by expressing  $p(\tau')$  in terms of  $P_{eq}(E)$ , the equilibrium energy distribution:

$$p(\tau') = P_{eq}(E) \frac{dE}{d\tau'} \propto n(E) e^{-E/T} \tau'^{-1} \propto n(E), \quad E = E_0 - T \ln(\tau'/\tau_0). \quad (13)$$

Substituting this into eq. (12) we get

$$\ln \chi''(\omega) = S(E) - \ln(\omega \tau_0) + \text{const.}, \quad E = E_0 + T \ln(\omega \tau_0) < E_0, \quad (14)$$

where eq. (6) has been used. In eq. (13) to each frequency corresponds an energy, and the loss peak frequency,  $\omega_m$ , corresponds to the average energy  $\bar{E}(T)$ . This is physically obvious, and it follows from eq. (14) and the definition of temperature:

$$T^{-1} = \left. \frac{\partial S}{\partial E} \right|_{E = \bar{E}(T)}. \quad (15)$$

In terms of  $\omega_m$ , eq. (14) may be rewritten as

$$\ln \chi''(\omega) = S(\bar{E}(T) + T \ln(\omega/\omega_m)) - \ln(\omega/\omega_m) + \text{const.} \quad (16)$$

Thus, measuring the dielectric loss is equivalent to measuring the function  $S(E)$  which determines the thermodynamics. As illustrated in fig. 2, when plotted in a log-log plot  $\chi''(\omega)$  is almost identical to  $S(E)$ .

A measurement of  $\tau(T)$  via eq. (7) yields  $\bar{E}(T)$  which, by means of eqs. (15) and (16), determines the dielectric loss.  $S(E)$  quite generally determines the linear response, but only if  $p(\tau')$  is broad does the simple expression given in eq. (16)

apply. For completeness, we now derive the generally valid expression for  $\chi(\omega)$ , assuming the high energy cut-off at  $E_0$  is irrelevant for thermodynamic properties. The partition function is then given by

$$Z(\beta) = \int_0^{\infty} n(E) e^{-\beta E} dE, \quad \beta = T^{-1}. \quad (17)$$

Introducing a dimensionless measure of the frequency by  $\tilde{\omega} = \omega \tau_0 e^{-\beta E_0}$ , the response function may be expressed in terms of the partition function as

$$\begin{aligned} \chi(\omega) &= \frac{\chi(0)}{Z(\beta)} \int_0^{\infty} \frac{n(E) e^{-\beta E} dE}{1 + i \tilde{\omega} e^{-\beta E}} = - \frac{\chi(0)}{Z(\beta)} \frac{1}{i \tilde{\omega}} \int_0^{\infty} n(E) \left( \sum_{j=1}^{\infty} (-i \tilde{\omega} e^{-\beta E})^j \right) dE \\ &= - \frac{\chi(0)}{Z(\beta)} \frac{1}{i \tilde{\omega}} \sum_{j=1}^{\infty} Z(j\beta) (-i \tilde{\omega})^j. \end{aligned} \quad (18)$$

This may be rewritten as a complex curve integral in the following way

$$\chi(\omega) = \frac{\chi(0)}{Z(\beta)} \frac{1}{2 \tilde{\omega}} \oint \frac{Z(s\beta) (i \tilde{\omega})^s}{\sin(s\pi)} ds \quad (19)$$

where the contour encircles the positive integers.

## 4. NON-LINEAR RELAXATION

In this section we study non-linear relaxation, i. e. relaxation towards thermal equilibrium from a state which is more than infinitesimally removed from equilibrium. This is a subject of great current interest [13,15,17,53,61,62] since it is important for applications of e. g. polymers, metallic glasses, or optical fibres, but also because it is a fascinating problem on its own to try to understand very slow relaxation of macroscopic properties in terms of motion on the atomic scale. The simplest models assume relaxation is due to a spectrum of activation energies for independent processes [53,61]. These models have considerable success. Basically, relaxation described by eq. (9) is also due to a distribution of activation energies but for processes which are interrelated by the requirement of conservation of probability.

The master equation has a unique stationary solution at any temperature, the canonical distribution, and at any given time the solution of the equation approaches the canonical distribution. This is true also if the temperature changes with time, as during the glass transition which is studied in the next section. Here we are concerned with the simpler case of relaxation at a constant temperature. Then the master equation may be solved by Laplace transformation in the following way. Defining as usual  $\tilde{P}(E,s) = \int_0^\infty P(E,t) \exp(-st) dt$  eq. (9) implies

$$s \tilde{P}(E,s) - P(E,0) = -\chi(E) \tilde{P}(E,s) + n(E) \int_0^{E_0} \chi(E') \tilde{P}(E',s) dE' \quad (20)$$

where  $P(E,0)$  is the energy distribution at  $t=0$  and  $\chi(E) = 1/\tau(E)$

has been introduced for convenience. Equation (20) implies

$$\tilde{P}(E, s) = \frac{n(E)}{\gamma(E) + s} \int_0^{E_0} \gamma(E') \tilde{P}(E', s) dE' + \frac{P(E, 0)}{\gamma(E) + s} \quad (21)$$

Multiplying both sides by  $\gamma(E)$  and integrating allows a determination of  $\int_0^\infty \gamma(E') \tilde{P}(E', s) dE'$ . When substituted into eq. (21) this gives

$$\tilde{P}(E, s) = \frac{n(E)}{\gamma(E) + s} \frac{\int_0^{E_0} \frac{\gamma(E') P(E', 0)}{\gamma(E') + s} dE'}{s \int_0^{E_0} \frac{n(E') dE'}{\gamma(E') + s}} + \frac{P(E, 0)}{\gamma(E) + s} \quad (22)$$

where use has been made of the fact that  $n(E)$  is normalised.  $P(E, t)$  is now calculated from  $\tilde{P}(E, s)$  as the inverse Laplace transform:

$$P(E, t) = \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \tilde{P}(E, s) e^{st} ds. \quad (23)$$

The evaluation of eq. (23) is discussed in the appendix.

Formally, the result is

$$P(E, t) = P_{eq}(E) + \int_0^{E_0} \frac{\int_0^{E_0} \frac{\gamma(E') P(E', 0)}{\gamma(E') - \omega(E'')} dE'}{\omega(E'') \int_0^{E_0} \frac{n(E') dE'}{(\gamma(E') - \omega(E''))^2}} \frac{n(E)}{\gamma(E) - \omega(E'')} e^{-\omega(E'')t} dE'' \quad (24)$$

where  $P_{eq}(E) \propto n(E) \exp(-E/T)$  is the normalised equilibrium solution, and  $\omega(E'')$  lies infinitely close to  $\gamma(E'')$  obeying

$$\int_0^{E_0} \frac{n(E') dE'}{\gamma(E') - \omega(E'')} = 0. \quad (25)$$

The solution of the master equation allows one to discuss energy relaxation in detail; other quantities relax similarly if they are functions of energy. As an example we consider a sudden quench at  $t=0$  from thermal equilibrium at temperature  $T_s$  to a lower temperature  $T$ . The time evolution of  $P(E)$  is monitored in fig. 3a where four snapshots of the thermalisation are shown. To get a better understanding of what happens it is convenient to introduce a characteristic energy,  $E_d$ , given by

$$E_d = E_0 - T \ln(t/\tau_0). \quad (26)$$

$E_d$  is the so-called demarcation energy which was introduced in the theory of thermalisation of photo-excited charge carriers in amorphous semiconductors [58,59]; a related quantity is used in relaxation theories based on a spectrum of activation energies [53,61,63,64]. The demarcation energy separates the low energy states, which have not jumped since  $t=0$ , from the higher energy states.  $P(E,t)$  may change below  $E_d$  only by increasing due to states arriving from above  $E_d$ . However, since the density of states is exponentially increasing, most jumps that arrive below  $E_d$  arrive just below  $E_d$ . So for all practical purposes one may think of  $P(E,t)$  as unchanged below  $E_d$ . Some time after the quench  $E_d$  reaches the  $t=0$  energy probability distribution which is an approximate gaussian.  $E_d$  then slides along the distribution until the equilibrium distribution is reached, where the distribution stops while  $E_d$  continues towards lower energies. According to eq. (26), the average energy relaxes logarithmically with time when the gaussian is slid along. Deviations from this is predicted for both short and long times where there is little change in energy. This kind of relaxation



behaviour is often found in experiment [53,61,65] and is referred to as  $\ln(t)$ -kinetics. It expresses the fact that the rate of glassy relaxation slows down as time goes by, a characteristic property of glassy relaxation. This fact is often rationalised by expressing the relaxation rate not only as a function of temperature, but also as a function of the so-called fictive temperature  $T_f$  [4,5,15,66,67]. By definition, the fictive temperature of a glass is the temperature where the equilibrium liquid has the same structure as the glass. In the present model  $T_f$  may be defined by

$$\bar{E}(T_f) = \int_0^{E_0} E P(E,t) dE \quad (27)$$

though there is no guaranty that  $P(E,t)$  is identical to the equilibrium distribution at  $T_g$ . The relaxation rate is a function of  $T_f$  in the present model simply because  $T_f$  determines the average activation energy for jumps. In the course of the relaxation process  $T_f$  decreases, implying the activation energy for jumps increases, which slows down the relaxation rate. Note that the straight line in figs. 1a and 1b illustrating glassy relaxation below  $T_g$  refers only to the initial stage of glassy relaxation, i. e. when  $T_f = T_g$ . In many cases, depending on the annealing temperature, one only observes this initial stage of the relaxation process, which in fig. 3a corresponds to the upper subfigure.

The relaxation in fig. 3a corresponds to the usual case of a glass relaxing below  $T_g$ . As another, more exotic example of relaxation we consider the opposite case, starting at thermal equilibrium at a the temperature  $T_g$  and then suddenly changing the temperature to  $T > T_g$ . This case is illustrated in fig.

3b. There is no gradual sliding of the energy probability distribution towards the equilibrium distribution. Instead, nothing happens as long as  $E_d$  is to the right of  $P_S(E)$ , the starting energy distribution, since all states are still frozen. When finally  $E_d$  reaches  $P_S(E)$ , the regions "evaporate" and thermalise almost immediately without visiting the states in between  $P_S(E)$  and  $P_{eq}(E)$ . This complex non-local behaviour reflects the fact that the master equation is not a differential equation. If the model is correct one may produce "dynamically generated" phase separation in a glass by annealing it for a long time, rising the temperature and then quenching it to low temperatures after just the right period of time.

## 5. THE GLASS TRANSITION

Solving the master equation for time-dependent temperature allows a study of the glass transition. In this case the equation is very complicated and cannot be solved by analytic methods. The same kind of problem is encountered in quantum-mechanics when the Hamiltonian is time-dependent. The only methods of solution is to step ahead in time with small increments, using a Hamiltonian which is changed for each time step. In our case, this may be done either by brute force stepping ahead in time  $\Delta t = T_0$ , or by taking larger time steps using the Laplace transform solution of sec. 4. The brute force method is not applicable for realistic laboratory time scales where the latter method is superior, but for purpose of illustration it works excellent. As an example we show in fig. 4 the specific heat  $c(t)$  calculated by brute force during cooling and subsequent reheating through the glass transition, where  $c(t)$  is defined by

$$c(t) = \frac{\frac{dE}{dt}}{\frac{dT}{dt}} \quad (28)$$

Fig. 4 is similar to experimental results which, however, also include a roughly temperature independent vibrational contribution to  $c(t)$ . The figure shows the well-known hysteresis effect. On reheating, the specific heat becomes negative for a while; this reflects a temporary decrease in energy due to relaxation from high energy states frozen-in during the cooling.

To study the glass transition more closely it is convenient to focus on the demarcation energy  $E_d$  which separates frozen

from non-frozen states.  $E_d$  has here a slightly different meaning than in sec. 3 : Suppose we cool the liquid at a constant rate to zero temperature in time  $t_0$  , from a state at high temperature where the average relaxation time is much smaller than  $t_0$  . The demarcation energy separates states that are frozen from now on from non-frozen states; it is given by  $E_d = E_0 - T(t) \ln(t_L/\tau_0)$  where  $t_L = t_0 - t$  is the time left till zero temperature is reached. In realistic cases the glass transition takes place for  $t_L$  of the same order of magnitude as  $t_0 \gg \tau_0$  , and  $t_L$  may be replaced by  $t_0$  in the expression for  $E_d$  since it enters only via a logarithm. We thus have

$$E_d = E_0 - T(t) \ln(t_0/\tau_0). \quad (29)$$

Note that  $E_d$  increases as time passes, while in sec. 4 it decreased. In thermal equilibrium the energy probability distribution is approximately a gaussian centred about  $\bar{E}(T)$  . As the temperature is lowered, the gaussian is displaced towards lower energies while  $E_d$  increases. When the gaussian meets  $E_d$  the glass transition takes place. This happens when  $\bar{E} = E_d$  . For a system of constant specific heat ,  $c$  , this condition implies

$$T_g = \frac{E_0}{c + \ln(t_0/\tau_0)} . \quad (30)$$

A linear relationship between  $1/T_g$  and the logarithm of the cooling rate is indeed often observed [9,68].

In a recent paper by the author the glass transition was studied by solving the master equation by brute force for systems with constant specific heat [46]. One finds two different kinds of glass transitions, depending on the rate of change with

temperature of  $E_d$  and of  $\bar{E}$ . The case when  $E_d$  changes much faster than  $\bar{E}$  was referred to as a slow glass transition since it requires long cooling times:  $\ln(t_0/\tau_0) \gg c$ . In this case the equilibrium gaussian almost doesn't move at all when  $E_d$  passes it and freezes-in the regions. The frozen-in energy distribution,  $P_0(E)$ , is just that corresponding to thermal equilibrium at  $T=T_g$ :

$$P_0(E) \cong \left(2\pi \langle (\Delta E)^2 \rangle^{-1/2}\right) \exp \left[ -\frac{(E-E_g)^2}{2 \langle (\Delta E)^2 \rangle} \right]. \quad (31)$$

Here  $E_g = cT_g$  and  $\langle (\Delta E)^2 \rangle = cT_g^2$ . Since the width of the gaussian is  $\sqrt{c} T_g$ , the width of the glass transition, determined from  $\Delta E_d = \sqrt{c} T_g$ , is given by

$$\frac{\Delta T_g}{T_g} = \frac{\sqrt{c}}{\ln(t_0/\tau_0)}. \quad (32)$$

A fast glass transition is the opposite limit, i. e. when  $\ln(t_0/\tau_0) \ll c$ . The demarcation energy then moves only very slowly compared to the gaussian, and  $E_d$  is almost constant during the glass transition. To determine  $P_0(E)$  we consider the energy fluctuations of a single region. As long as its energy is above  $E_d$  it jumps many times between the high energy states (remember  $n(E)$  is exponentially increasing). Sooner or later, however, the region ends up in a state below  $E_d$ , or just above  $E_d$  being subsequently frozen when  $E_d$  passes. As all other jumps, the last jump hits an energy with probability  $n(E)$ . Around  $E_g$   $n(E)$  is proportional to  $\exp(E/T_g)$ , so  $P_0(E)$  is roughly given by

$$P_0(E) \approx \begin{cases} T_g^{-1} \exp[(E-E_g)/T_g] , & E < E_g \\ 0 & , E > E_g \end{cases} \quad (33)$$

The predicted exponential increase of  $P_0(E)$  below  $E_g$  was confirmed in the numerical solution of the master equation of ref. [46]. However, above  $E_g$   $P_0(E)$  does not drop discontinuously to zero but seems rather to follow a gaussian decay. We have not been able to prove this analytically. Neither have we been able to calculate the temperature width of the fast glass transition.

An important thing to be learnt from this study of the glass transition is that, in general, one cannot expect a glass merely to have the structure of the equilibrium liquid at  $T=T_g$ . Certainly, the average frozen-in energy is equal to the average energy of the equilibrium liquid at  $T_g$ , but the distribution of energies in the glass may be different from that corresponding to the equilibrium liquid at  $T_g$ . This has important consequences for glass properties affecting e. g. glassy relaxation. Any physical property which is a function of  $E$  will, if it depends linearly on  $E$  for the relevant energies, also be distributed according to a gaussian or an exponential, depending on the cooling rate through the glass transition. For instance, amorphous semiconductors prepared by a fast glass transition are likely to have exponential band tails of localised states [46,69]. Note that, since the cooling rate must be compared to the region specific heat at the glass transition which depends on the size of a region, there is no absolute measure on the cooling rate determining the kind of glass transition.

The usual way of producing glasses is by cooling the liquid

at a more or less constant rate from a high temperature where the viscosity is low, corresponding to an average relaxation time much shorter than the cooling time. This process is usually referred to as a glass transition. However, glasses may also be prepared in another way, namely by a sudden cooling of the liquid from a state of thermal equilibrium at a temperature where the average relaxation time is large compared to the cooling time. This may be referred to as a "quench" since the regions are frozen-in instantaneously and do not have time to jump. Glasses produced by a quench obviously have an energy distribution equal to that of the liquid at the "freezing" temperature. Thus, a quench and a slow glass transition yields a gaussian distribution of frozen-in energies in the glass, while a fast glass transition, though corresponding to cooling rates in between that of a quench and of a slow glass transition, results in an exponential distribution of region energies.

## 6. SUMMARY AND DISCUSSION

Like most preceding models, the present model of viscous liquids is based on the idea that viscous flow takes place via sudden flow events, rather than in a continuous manner. A flow event is localised to a group of atoms referred to as a region, and the liquid is then regarded as an ensemble of non-interacting regions. This assumption is not easily justified. A region is small, perhaps 10-20 Å in linear dimension [70], and therefore it has large surface energy which is likely to depend on the states of the surrounding regions. Furthermore, the liquid is not literally divided into regions, so the picture certainly is oversimplified. The assumption of non-interacting regions also rules out an explanation of the mechanism of viscous flow which must involve interaction between the regions. Despite all this it is hoped that the picture proposed here, by focusing on the flow event activation energy, does catch the essential physics of viscous liquids and the glass transition.

Most glass forming liquids have a strikingly non-Arrhenius temperature dependence of the viscosity. The simplest explanation for this is to assume the activation energy of the viscosity is temperature dependent. The curvature in the Arrhenius plot implies  $\Delta E$  increases as  $T$  decreases. Writing  $\Delta E = E_0 - \bar{E}$  this is easily understandable in the region picture since the average region energy  $\bar{E}$  must decrease as  $T$  decreases. This idea, which has here been somewhat oversimplified, is the basis of the theory proposed in the present paper; it goes back to Goldstein [29]. A similar line of thought has also been made use of by Morito and Egami in a discussion of mechanical relaxation in metallic glasses [71].



The idea allows a very simple explanation of glassy relaxation as having, in its initial stage (which is often the only accessible), a constant temperature independent activation energy equal to  $E_0 - \bar{E}(T_g)$ .

Experiments on the pressure dependence of the liquid average relaxation time are consistent with the region picture. One finds that  $\ln(\tau)$  is not a linear function of pressure. Instead it curves in way which implies the activation volume,  $\Delta V$ , increases as the pressure increases [72], which is easy to understand in the region picture. Writing  $\Delta V = V_0 - \bar{V}$ , it implies the average region volume decreases as the pressure increases, as is required by thermodynamics.

The very small preexponentials for  $\tau$ , which are observed close to the glass transition, have always been a matter of concern. The preexponential is often of order  $10^{-50}$  s or even  $10^{-100}$ , which, according to the conventional interpretation, indicates a large entropy of activation. As shown in sec. 2 this interpretation is problematic: If  $\tau$  is expressed in terms of  $\Delta E(T)$  and  $\Delta S(T)$  by eq. (3),  $\Delta E(T)$  is generally not the slope in the Arrhenius plot and thus the preexponential is not  $\exp(-\Delta S)$ . In the present theory  $\Delta S=0$  is assumed, and the preexponential is  $\exp(-c(T))$  where  $c(T)$  is the region specific heat. The fact that large  $c$ 's are needed to fit experiment is consistent with the basic idea that a region is a thermodynamic system, i. e. has many degrees of freedom. The curvature in the Arrhenius plot implies  $c(T)$  increases as  $T$  decreases towards  $T_g$ . This is indeed often the case in measurements of the excess specific heat of the liquid relative to the crystal [20]. According to the model,  $c$  goes to zero as  $T$  approaches the melting temperature. This is not seen in

thermodynamic measurements and is probably due to a gradual breakdown of the whole approach as the less viscous regime is entered.

A straight line in the Arrhenius plot is usually thought of as indicating thermal activation with a single activation energy. In the model proposed here, however, this is only true if  $c=0$ . Generally, a straight line indicates a constant region specific heat. The slope of the line is not the activation energy but the zero temperature activation energy, and the preexponential is  $\exp(-c)$ . This suggests an alternative explanation for the anomalously large attack frequencies sometimes found in rate processes, e. g. in diffusion [73]. While usually interpreted as indicating large activation entropies, these anomalous preexponentials may instead be due to processes involving the excitement of a system with many degrees of freedom.

Brawer has proposed a detailed model for flow events based on insights gained from computer simulations [13,47]. In his model a region is composed of  $K$  volume elements, each of which can take two possible densities. The region energy is a function of the number of low density volume elements,  $n$ , such that large  $n$  implies large energy. A flow event occurs when a region is excited to energy  $E_0$ ; this energy corresponds to a state with  $N > n$  low density volume elements. The number of ways such a state may be reached depends on the value of  $n$ , and entropy effects are thus important in the theory. For instance, the curvature of  $\ln(\tau)$  in the Arrhenius plot is due to the fact that, as the temperature increases, there are fewer and fewer different ways to excite a region to the critical  $N$ , resulting in a weaker temperature dependence of  $\tau$  [13]. Similarly, the small preexponentials arise from the large entropy of activation

inherent in the cooperative nature of the flow event [13].

Brawer's model differs from the one proposed here which focuses entirely on the activation energy. The assumption  $\Delta S=0$  is here made to simplify the theory. This assumption is hard to justify if the transition state is a non-vibrational state corresponding to the less viscous liquid, as has been proposed by Goldstein [29]. A constant activation entropy seems more likely. This corresponds simply to a change of  $\tau_0$ , and may easily be incorporated into the model. The model then does not apply in the whole liquid temperature range, and the beginning of the curvature in the Arrhenius plot must be regarded as signaling a transition from the low viscosity liquid described by standard liquid theory to the really viscous liquid where the present theory applies.

The dynamics governing the fluctuations of region energy is given by the master equation eq. (9). It was derived assuming that, once excited into the transition state, a region has completely forgotten where it came from. Actually, this must be true if one assumes there is only one transition state. The master equation allows a detailed study of linear and non-linear relaxation phenomena, as well as of the glass transition. This follows Goldstein's program according to which the glass transition and the glassy states are easily understood once a theory of viscous liquids is arrived at [29,36].

From his picture of flow events, Brawer derived a kinetic equation for the region energy fluctuations. The equation reflects the fact that in his model there are many transition states. An excited region has not entirely forgotten where it came from and may not end up in any other state: A transition state is a state with  $N$  out of  $K$  volume elements being low

density volume elements. From such a state it is not possible directly to reach any state with  $n < N$  low density volume elements. Thus, Brawer's equation is not equivalent to eq. (9), in contrast to what was previously stated [46]. Equation (9) is more related to Goldstein's brief 1972 discussion of the kinetics of flow events [29]. He never developed this further, however, being more concerned with explaining  $\beta$ -relaxation, which, if to be explained by the same mechanism as the dominant  $\alpha$ -relaxation, is inconsistent with a thermodynamic density of states.

At any temperature there is a spread in region energies which gives rise to a distribution of activation energies and thereby a distribution of relaxation times. It is a very old idea to explain distributions of relaxation times by assuming a spectrum of activation energies, but usually this is assumed for unspecified independent processes. Here, the spectrum of activation energies arise for processes which are not independent, being related by the requirement of conservation of probability: at any time a region must be in some state.

A measurement of  $\tau(T)$  allows a determination of the density of states  $n(E)$ , which is essentially the only input to the master equation, and from which it is thus possible to predict all linear and non-linear relaxation phenomena. According to the theory, a true Arrhenius  $\tau(T)$  (i. e. with a preexponential of order 1 picosecond) implies a single relaxation time, while deviations from true Arrhenius behaviour imply a distribution of relaxation times. This is in agreement with experiment [12,74], though there are exceptions to the general tendency [75]. If the size of the regions is assumed to be independent of the liquid, we furthermore predict the excess specific heat per unit volume to correlate to the non-Arrhenius

behaviour. This also agrees with experiment [12]. Things look worse when it comes to a quantitative comparison of theory and experiment. The observed very small preexponentials imply a large region specific heat, typically between 20 and 200. From eq. (14) it is easy to show that the half-width of the loss peak is  $2\sqrt{2c}/\ln(10)$  decades which gives half-widths between 5 and 17 decades. The actual half width of the  $\alpha$ -peak, however, is always between 2 and 3 decades [49,72], and this is a serious discrepancy. We know of no likely explanation for it nor of any extension of the theory to account for it. It must be concluded that at present the theory is incomplete.

By solving the master equation, non-linear relaxation may be monitored in time. One finds an asymmetry between relaxation from high to low energies which is continuous (fig. 3a), and the converse process which is almost discontinuous (fig. 3b). If the theory is correct the latter process may be applied to produce "dynamically generated" phase separation in glasses by interrupting the relaxation at just the right time via a quench to low temperature.

In the study of glassy relaxation it has always been a mystery that the relaxation takes place much faster than expected from an extrapolation of the equilibrium relaxation rate. In the present model, this is because glassy relaxation proceeds with activation energy  $\Delta E = E_0 - \bar{E}(T_g)$  which is lower than  $\Delta E$  for the equilibrium liquid below  $T_g$ . This is true for the initial stage of glassy relaxation. In his model Brawer explains sub- $T_g$  relaxation as the occurrence of flow events only in the highly excited states [13]. In a sense this is true also for the present model, but the point is that all regions of the glass are highly excited compared to the equilibrium liquid and that all

regions may participate in the relaxation, it still having the same low activation energy.

The theory predicts there are two different kinds of glass transition, slow and fast. A slow glass transition freezes-in the equilibrium energy probability distribution at  $T_g$ . Things are more complicated in the case of a fast glass transition where relaxation phenomena at  $T_g$  become important. The lowest lying states freeze while the higher lying states have time to relax, and the resulting frozen-in energy distribution is quite different from the equilibrium distribution. It is usually assumed a glass has just the structure of the equilibrium liquid at  $T_g$ , but the model shows that this does not have to be so. After all, glassy relaxation has been known for years and since relaxation right at  $T_g$  is much faster, it cannot be ruled out a priori that this might affect the structure of a glass. -- A third way to produce glasses from liquids is via a quench, an "infinitely" fast cooling which really has little in common with a glass transition. Like a slow glass transition, a quench results in a gaussian distribution of frozen-in energies in the glass (or of any other quantity linearly related to  $E$ ), while a fast glass transition results in an exponential distribution of frozen-in energies, as shown in sec. 5 and ref. [46].

According to the model, the glass transition is a purely kinetic phenomenon which is not due to an underlying phase transition. This does not mean, however, that the behaviour of  $\ln(\tau)$  above  $T_g$  is expected to extrapolate to low temperatures. Since a region contains only a finite number of states, one has  $c(T) \rightarrow 0$  as  $T \rightarrow 0$ , the analogue of the Nernst theorem. Thus, eventually the preexponential for  $\tau$  of the equilibrium liquid must return to one picosecond on cooling,

i. e. a change of sign is predicted for the second derivative of  $\ln(\tau)(T^{-1})$ . And this must actually happen not very far below  $T_g$  if the Kauzmann paradox is to be avoided. We know of no experiments indicating this, but it is to be noted that for many solids the preexponential stops decreasing and becomes almost constant close to  $T_g$ . Similarly, we predict a change of sign of the second derivative of  $\ln(\tau)(p)$  due to the fact that  $V > 0$ . This may be easier to check experimentally by choosing a suitable temperature for the experiment.

## ACKNOWLEDGEMENT

This work was supported by the Danish Natural Science Research Council. It was finished while the author was a visiting scholar at Department of Materials Engineering, Rensselaer Polytechnic Institute, New York. I wish to thank Prof. Moynihan and his group for their kind hospitality and for many useful discussions while writing the paper. Back home in Roskilde I wish to thank T Christensen and N B Olsen who learnt me a lot about the glass transition during the last 5 years.



## APPENDIX: SOLVING THE MASTER EQUATION

We here derive eq. (24) and discuss briefly how to calculate the solution numerically. The master equation is solved for constant temperature; if the temperature varies in time the solution given below may be iterated by stepping ahead small time steps for a constant temperature. The discrete version of the master equation is considered. Writing  $E_i = (i/N)E_0$  ( $i=1, \dots, N$ ), the master equation is

$$\frac{dP_i}{dt} = -\gamma_i P_i + n_i \sum_{j=1}^N \gamma_j P_j, \quad (A1)$$

where  $P_i = P(E_i)$ ,  $\gamma_i = \gamma(E_i)$ , and  $n_i$  is the density of states at  $E_i$  normalised so that  $\sum_{i=1}^N n_i = 1$ . The solution of eq. (A1) is (compare eqs. (22) and (23))

$$P_i(t) = \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \tilde{P}_i(s) e^{st} ds, \quad (A2)$$

where

$$\tilde{P}_i(s) = \frac{n_i}{s(\gamma_i + s)} \frac{\sum_{j=1}^N \frac{\gamma_j P_j(0)}{\gamma_j + s}}{\sum_{j=1}^N \frac{n_j}{\gamma_j + s}} + \frac{P_i(0)}{\gamma_i + s}. \quad (A3)$$

The integration contour in eq. (A2) is by definition displaced slightly to the right of the imaginary axis. The integral may be calculated by including an infinitely large semicircle surrounding the left half-plane, which closes the integration contour so that the residue theorem may be applied. There are  $N$  poles, corresponding to the  $N$  eigenvalues of the "Hamiltonian"

matrix:  $-\gamma_i \delta_{ij} + n_i \gamma_j$ . For master equations in general, all eigenvalues are negative real numbers except one which is zero. It is easy to see that the residue at  $s=0$ , corresponding to the zero eigenvalue, is equal to the normalised thermal equilibrium solution given by the canonical ensemble,  $P_{i,eq} \propto n_i/\gamma_i$ . The remaining eigenvalues,  $-\omega_k$  ( $k=1, \dots, N-1$ ), are determined from the equation

$$\sum_{j=1}^N \frac{n_j}{\gamma_j - \omega_k} = 0 \quad (A4)$$

and obey

$$\gamma_k < \omega_k < \gamma_{k+1} \quad (A5)$$

Note that there is no pole at  $s=-\gamma_i$  since this singularity is cancelled by the second term of eq. (A3). The residue at  $s=-\omega_k$  is easily found by the standard rules, and the final solution is

$$P_i(t) = P_{i,eq} + \sum_{k=1}^{N-1} \frac{n_i}{\omega_k (\gamma_i - \omega_k)} \frac{\sum_{j=1}^N \frac{\gamma_j P_j(0)}{\gamma_j - \omega_k}}{\sum_{j=1}^N \frac{n_j}{(\gamma_j - \omega_k)^2}} e^{-\omega_k t} \quad (A6)$$

which proves eq. (24). The normalisation of  $P_i$  is maintained by virtue of eq. (A4).

In the evaluation of eq. (A6) one must find the eigenvalues from eq. (A4). It is not wise to use the Newton-Raphson method which may shoot one out of the interval eq. (A5). It is better simply repeatedly to half the interval. At low energies  $\omega_k$  is very close to  $\gamma_k$  and large numerical errors easily arise for the term  $1/(\gamma_k - \omega_k)$  in eq. (A6) which instead may be evaluated from

eq. (A4):

$$\frac{1}{\gamma_k - w_k} \approx \frac{1}{n_k} \sum_{\substack{j=1 \\ j \neq k}}^N \frac{n_j}{\gamma_j - \gamma_k} \quad (A7)$$

To avoid overflow problems in calculating eq. (A6), it is advisable to identify the leading term in each sum, factorise it and rewrite all products as e. g.  $ab = \exp(\ln(a) + \ln(b))$ .

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## FIGURE CAPTIONS

Fig. 1 : Determination of the activation energy of a flow event from an Arrhenius plot of the average relaxation time  $\tau$ .  $\tau$  may be determined e. g. from viscosity measurements. Above  $T_g$   $\tau$  is non-Arrhenius while below  $T_g$  it becomes Arrhenius. Fig. 1a shows the naive interpretation of data, according to which the slope of the tangent is the activation energy and the "preexponential" of  $\tau$  is  $\exp(-\Delta S)$  where  $\Delta S$  is the activation entropy. There is a discontinuous decrease in activation energy at  $T_g$  which is traditionally explained as due to the vanishing below  $T_g$  of the contribution from structural changes to  $\Delta E$ . Fig. 1b shows the interpretation of data proposed here which is based on assuming  $\Delta S=0$ . The activation energy is then the slope of the secant drawn from  $(0, \ln(\tau_0))$  to  $(T^{-1}, \ln(\tau))$  where  $\tau_0$  is the high temperature limit of  $\tau(T)$  (about 1 picosecond). Even in this interpretation does the activation energy increase as the temperature decreases. But at the glass transition there is no change of  $\Delta E$ , instead what happens is that  $\Delta E$  stops changing with temperature and becomes constant. In this interpretation the preexponential is  $\exp(-c(T))$  which follows from the fact that the slope of the tangent is  $\Delta E(T) + Tc(T)$  (eq. (8)).

Fig. 2 : Connection between the entropy function  $S(E)$  and the dielectric loss peak, valid whenever the distribution of relaxation times is broad. Fig. 2a shows  $S(E)$ . By definition of temperature the tangent at  $E=\bar{E}(T)$  has slope  $T^{-1}$ . Fig. 2b shows the loss peak in a log-log plot constructed from fig. 2a by means of eq. (15). The loss peak frequency corresponds to  $\bar{E}(T)$ .



Fig. 3 : Relaxation towards equilibrium after a quench from high to low temperature (a), and from low to high temperature (b). Each figure shows four snapshots of the energy probability distribution. The dots mark the equilibrium distribution and the line shows the demarcation energy  $E_d$  given by eq. (26). Below  $E_d$  states are frozen and  $P(E)$  changes only little. Fig. 3a corresponds to the usual case of glassy relaxation. Here  $E_d$  catches the energy distribution and slides it along until the equilibrium distribution is reached. Fig. 3b corresponds to a sudden heating of a well annealed glass. When  $E_d$  reaches the starting distribution, states around  $E_d$  jump and then almost immediately thermalise, without visiting the states in between  $E_d$  and  $\bar{E}(T)$ . This peculiar behaviour is possible because the master equation is non-local and is not a differential equation. If the relaxation is interrupted at the right time by quenching to low temperature, one ends up with a "dynamically generated" phase separated glass. The system studied in fig. 3 has  $n(E) \propto E^{19}$  and the low and high temperatures are  $0.025 E_0$  and  $0.040 E_0$  respectively.

Fig. 4 : Specific heat as function of temperature for a cooling at constant rate from thermal equilibrium to zero temperature and a subsequent reheating. The dotted curve is the thermal equilibrium specific heat. During cooling the specific heat has the equilibrium value at high temperatures, but goes to zero at low temperatures because the states freeze-in. On reheating, the specific heat becomes slightly negative, corresponding to a decrease in average energy though the temperature increases. This is due to relaxation from frozen-in states at relatively

high energies which becomes possible when the temperature is not too low. Note that the specific heat exhibits hysteresis, a phenomenon which is due to the kinetic nature of the glass transition and which has been seen in numerous experiments. The figure was generated by solving the master equation by brute force for a system with  $n(E) \propto E^4$ , stepping ahead in time a step of  $\tau_0$ . The starting temperature was  $0.25 E_0$  and the cooling time to zero temperature was  $5000 \tau_0$ .

Fig. 5 : Different ways of reaching the glassy state. A glass may be produced by a glass transition or by a quench. A glass transition is cooling in a time much longer than the average relaxation time of the liquid at the beginning of the cooling. In this case there is a gradual falling out of equilibrium during the cooling. According to the theory there are two different kinds of glass transitions, slow and fast, depending on whether  $\ln(t_0/\tau_0)/c_g$  is much larger or much smaller than one, where  $t_0$  is the cooling time,  $\tau_0$  is 1 picosecond, and  $c_g$  is the region specific heat at  $T_g$  in units of Boltzmann's constant. A quench is the opposite of a glass transition, i. e. when the cooling is much faster than the liquid average relaxation time. A quench immediately freezes the energy probability distribution. As shown in the text, a quench and a slow glass transition both result in a gaussian frozen-in energy distribution. A fast glass transition, though arising for cooling rates in between, results in an exponentially increasing, abruptly decreasing frozen-in energy distribution. In this case relaxation phenomena right at the glass transition are important.

Fig 1a

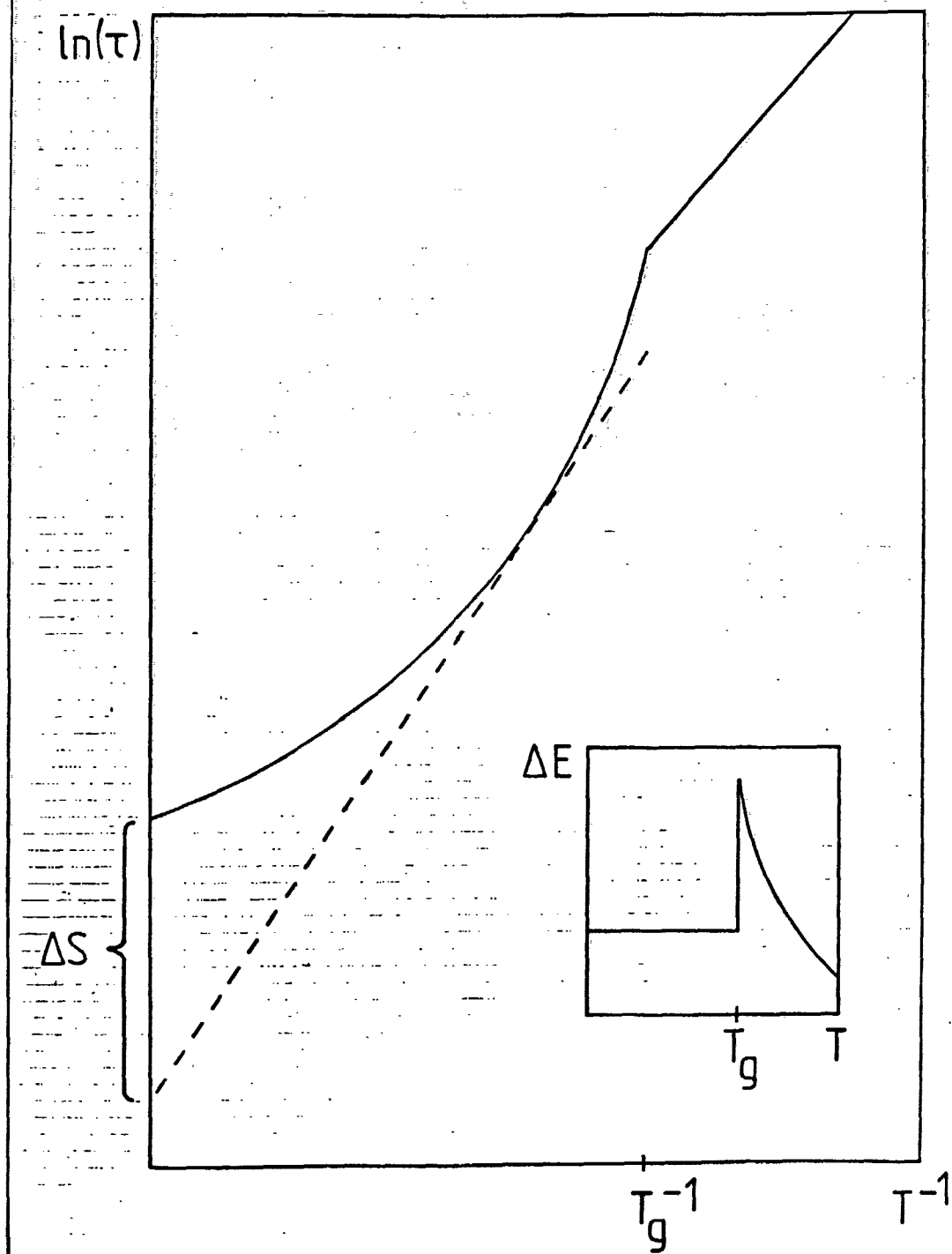


Fig 1b

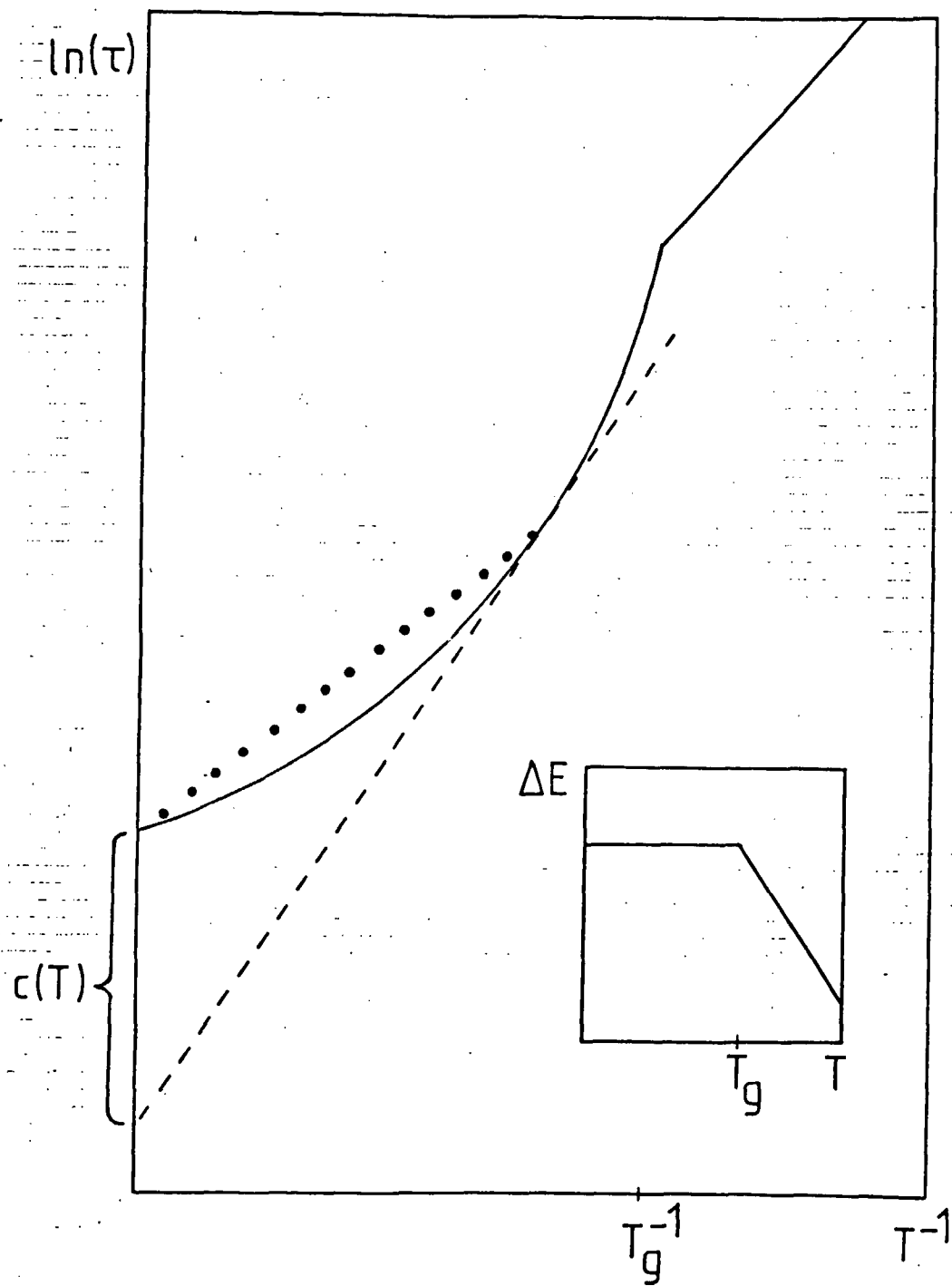


Fig 2a

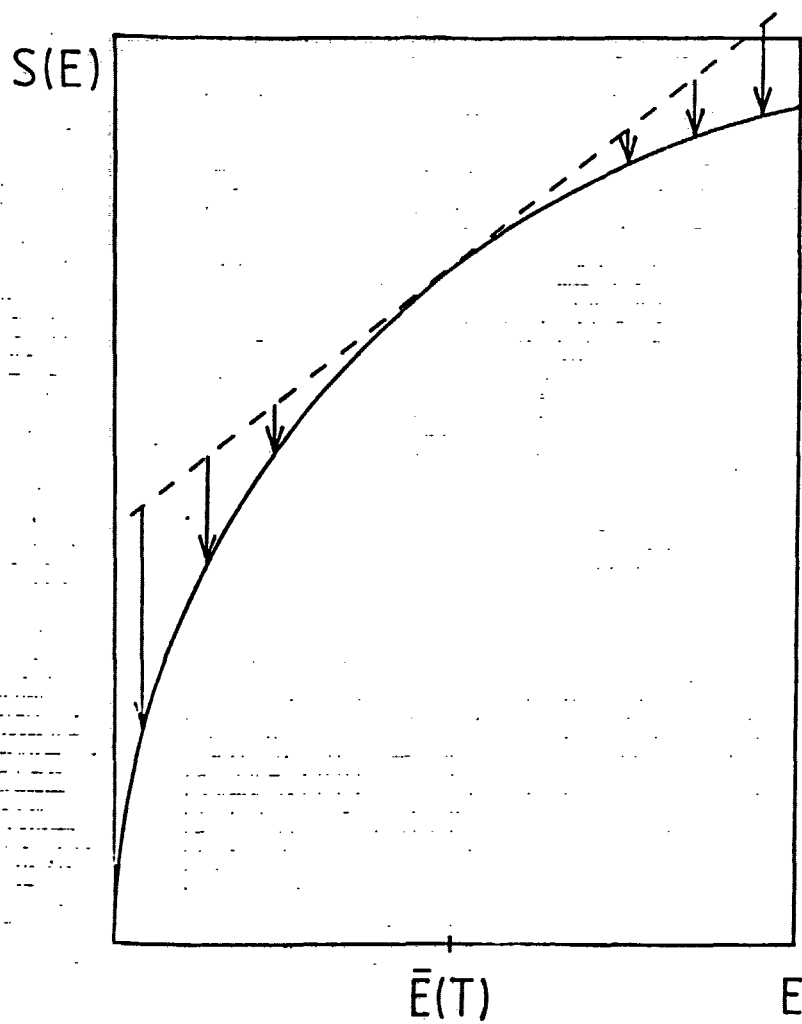
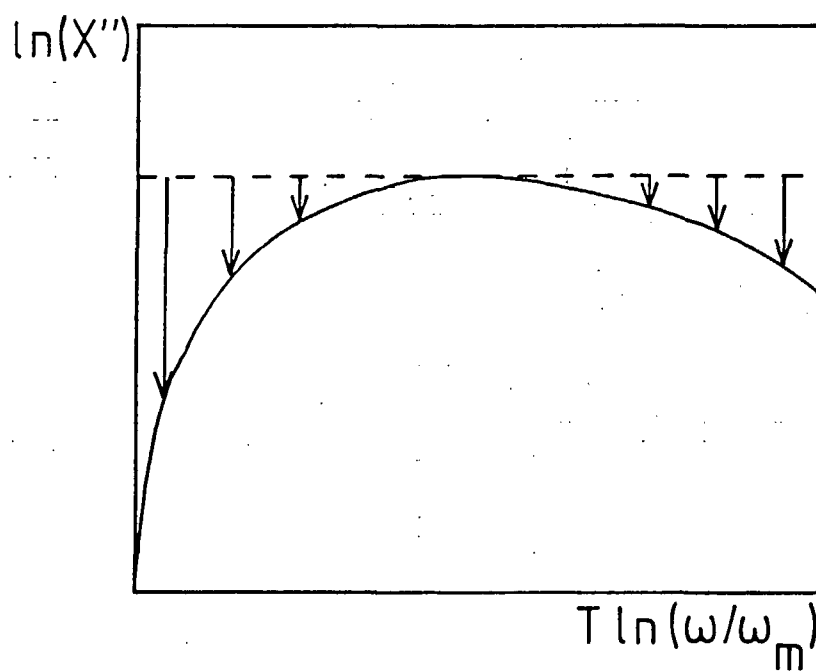


Fig 2b



... *just as expected*  
xx *probable* ..

Fig. 3a

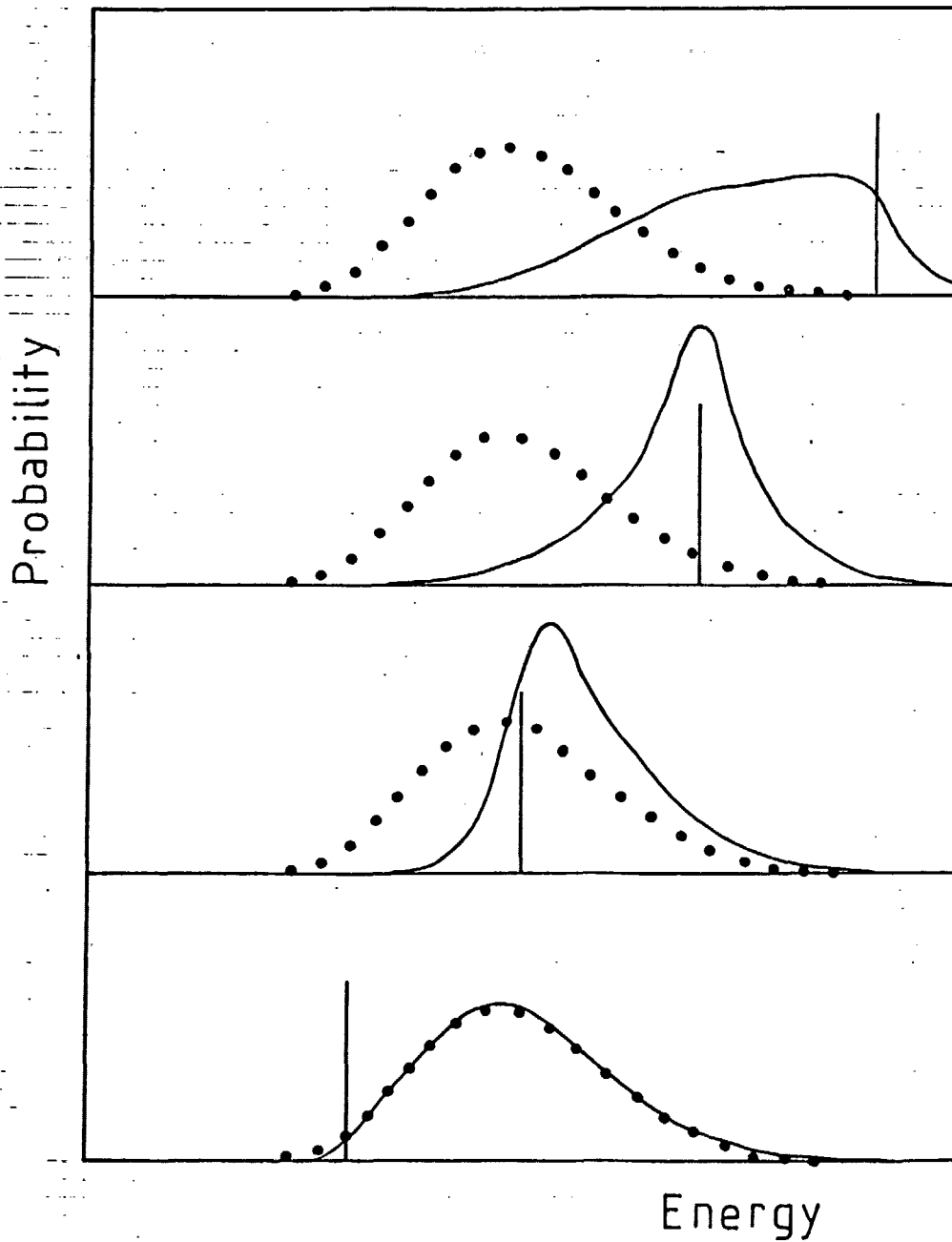
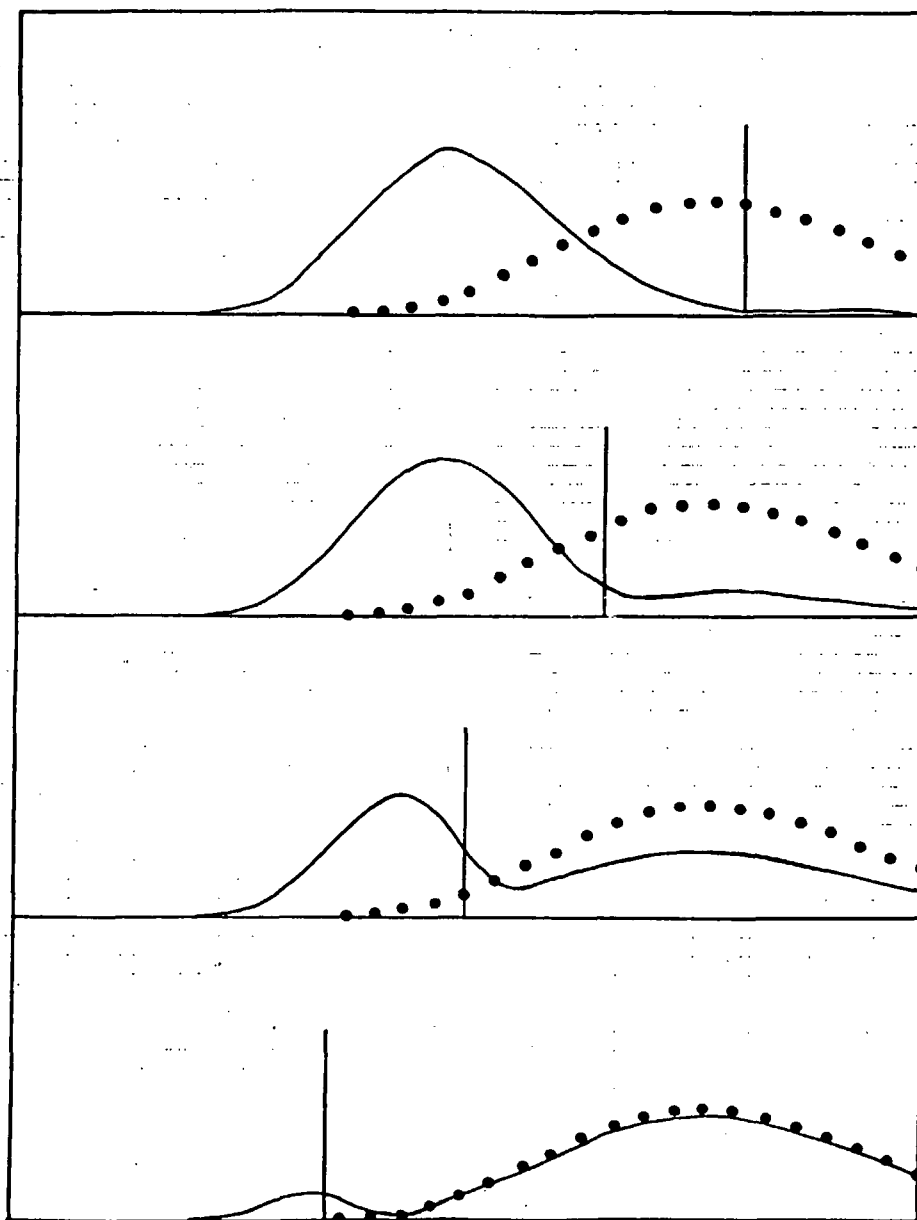


Fig. 3b

• • • full potential  
x x particles under ... (attracted to ...)

Probability



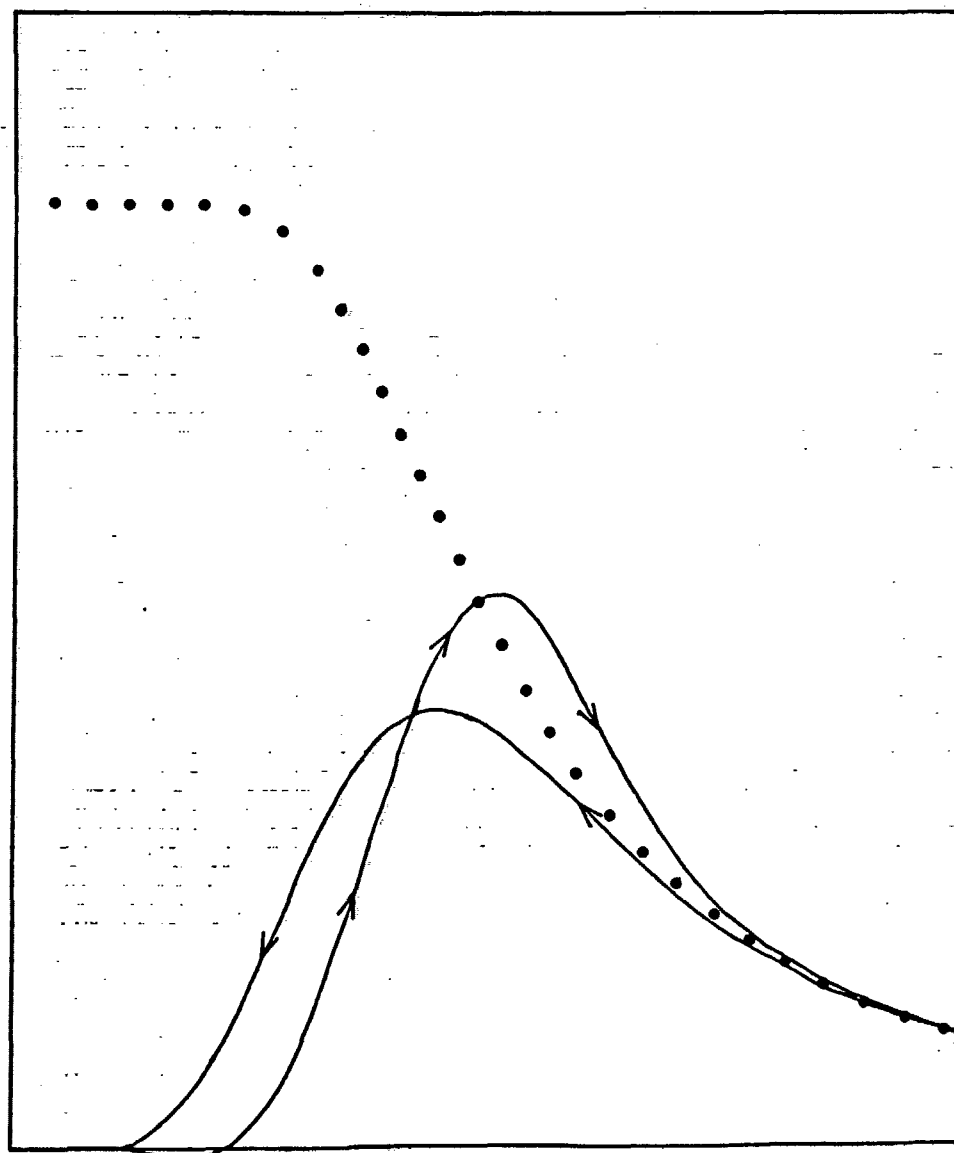
Energy



Fig 4

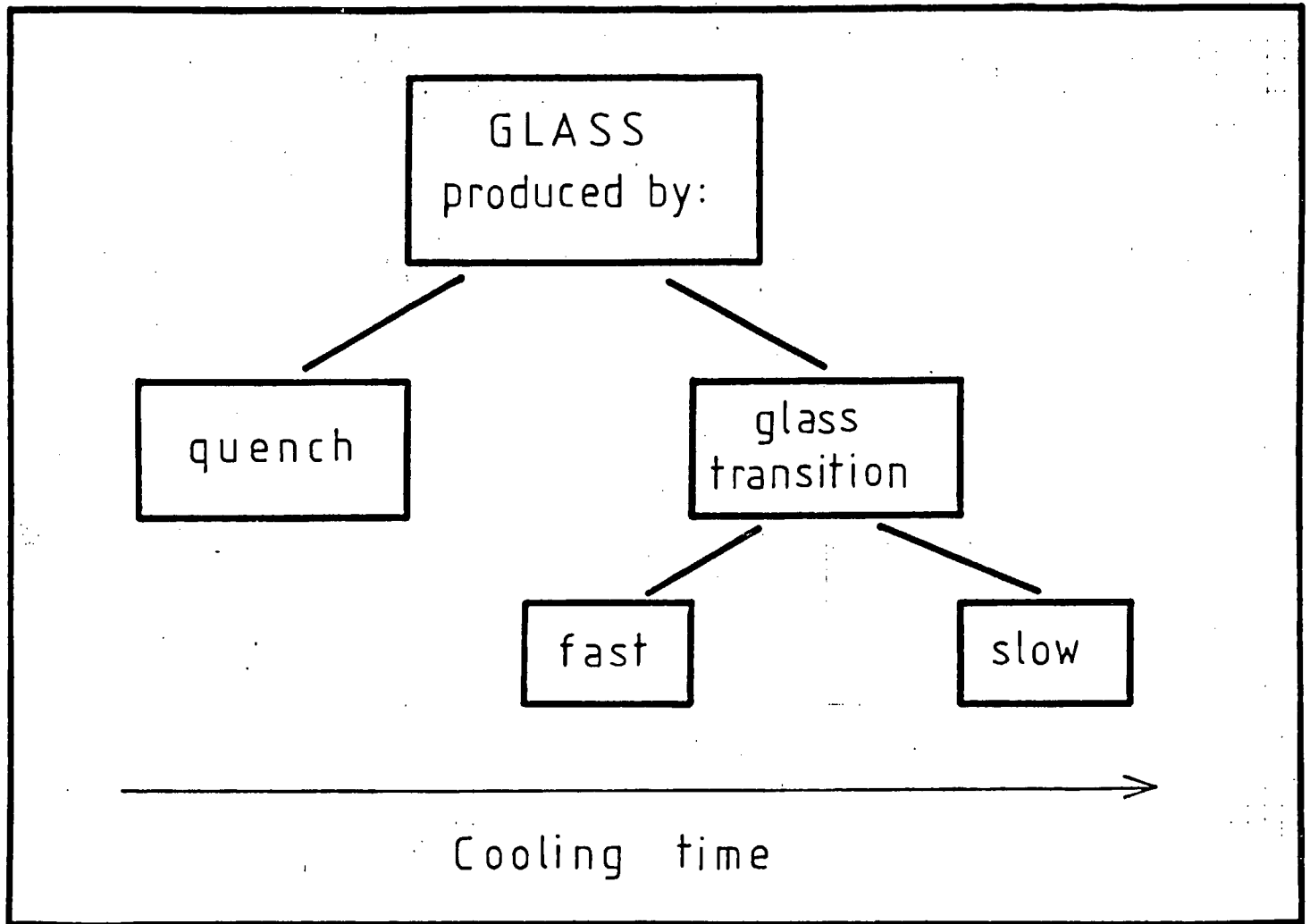
..  $\mu H$   $\Delta T$  ..  
X  $\mu H$   $\Delta T$  ..

Specific heat



Temperature

Fig 5





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Samtlige opgaver stillet i tiden 1974-jan. 1986.
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Authors: M.B.El-Den, N.B.Olsen, Ib Høst Pedersen, Petr Visčor
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Projektrapport af Frank Colding Ludvigsen  
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Fysik: Jens Højgaard Jensen
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Af: Jeppe Dyre  
Vejledere: Niels Boye Olsen og Peder Voetmann Christiansen.
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Af: Iben Maj Christiansen  
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138/87 "JOSEPHSON EFFECT AND CIRCLE MAP."

Paper presented at The International Workshop on Teaching Nonlinear Phenomena at Universities and Schools, "Chaos in Education". Balaton, Hungary, 26 April-2 May 1987.

By: Peder Voetmann Christiansen

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by: Bernhelm Booss-Bavnbek  
Krzysztof P. Wojciechowski

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Martin Bohle-Carbonell

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Projektrapport af Finn C. Physant  
Vejleder: Ib Thiersen

142/87 "The Calderón Projektor for Operators With Splitting Elliptic Symbols"

by: Bernhelm Booss-Bavnbek og  
Krzysztof P. Wojciechowski

143/87 "Kursusmateriale til Matematik på NAT-BAS"

af: Mogens Brun Heefelt

144/87 "Context and Non-Locality - A Peircan Approach"

Paper presented at the Symposium on the Foundations of Modern Physics The Copenhagen Interpretation 60 Years after the Como Lecture. Joensuu, Finland, 6 - 8 august 1987.

By: Peder Voetmann Christiansen

145/87 "AIMS AND SCOPE OF APPLICATIONS AND MODELLING IN MATHEMATICS CURRICULA"

Manuscript of a plenary lecture delivered at ICMTA 3, Kassel, FRG 8.-11.9.1987

By: Mogens Niss

146/87 "BESTEMMELSE AF BULKRESISTIVITETEN I SILICIUM"

- en ny frekvensbaseret målemetode.

Fysikspeciale af Jan Vedde

Vejledere: Niels Boye Olsen & Petr Višćor

147/87 "Rapport om BIS på NAT-BAS"

redigeret af: Mogens Brun Heefelt

148/87 "Naturvidenskabsundervisning med Samfundsperspektiv"

af: Peter Colding-Jørgensen DLH  
Albert Chr. Paulsen

149/87 "In-Situ Measurements of the density of amorphous germanium prepared in ultra high vacuum"

by: Petr Višćor

150/87 "Structure and the Existence of the first sharp diffraction peak in amorphous germanium prepared in UHV and measured in-situ"

by: Petr Višćor

151/87 "DYNAMISK PROGRAMMERING"

Matematikprojekt af:  
Birgit Andresen, Keld Nielsen og Jimmy Staal  
Vejleder: Mogens Niss